Green chemistry

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Green chemistry, also called **sustainable chemistry**, is an area of chemistry and chemical engineering focused on the designing of products and processes that minimize the use and generation of hazardous substances.[1] Whereas environmental chemistry focuses on the effects of polluting chemicals on nature, green chemistry focuses on technological approaches to preventing pollution and reducing consumption of nonrenewable resources.[2][3][4][5][6][7]

Green chemistry overlaps with all subdisciplines of chemistry but with a particular focus on chemical synthesis, process chemistry, and chemical engineering, in industrial applications. To a lesser extent, the principles of green chemistry also affect laboratory practices. The overarching goals of green chemistry—namely, more resource-efficient and inherently safer design of molecules, materials, products, and processes—can be pursued in a wide range of contexts.

Contents

History

Green chemistry emerged from a variety of existing ideas and research efforts (such as atom economy and catalysis) in the period leading up to the 1990s, in the context of increasing attention to problems of chemical pollution and resource depletion. The development of green chemistry in Europe and the United States was linked to a shift in environmental problem-solving strategies: a movement from command and control regulation and mandated reduction of industrial emissions at the "end of the pipe," toward the active prevention of pollution through the innovative design of production technologies themselves. The set of concepts now recognized as green chemistry coalesced in the mid- to late-1990s, along with broader adoption of the term (which prevailed over competing terms such as "clean" and "sustainable" chemistry).[8][9]

In the United States, the Environmental Protection Agency played a significant early role in fostering green chemistry through its pollution prevention programs, funding, and professional coordination. At the same time in the United Kingdom, researchers at the University of York contributed to the establishment of the Green Chemistry Network within the Royal Society of Chemistry, and the launch of the journal *Green Chemistry*.[9]

Principles

In 1998, Paul Anastas (who then directed the Green Chemistry Program at the US EPA) and John C. Warner (then of Polaroid Corporation) published a set of principles to guide the practice of green chemistry.[10] The twelve principles address a range of ways to reduce the environmental and health impacts of chemical production, and also indicate research priorities for the development of green chemistry technologies.

The principles cover such concepts as:

- the design of processes to maximize the amount of raw material that ends up in the product;
- the use of renewable material feedstocks and energy sources;
- the use of safe, environmentally benign substances, including solvents, whenever possible;
- the design of energy efficient processes;
- avoiding the production of waste, which is viewed as the ideal form of waste management.

The **twelve principles of green chemistry** are:

1. It is better to prevent waste than to treat or clean up waste after it is formed.
2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. Chemical products should be designed to preserve efficacy of function while reducing toxicity.
5. The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.

6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
7. A raw material or feedstock should be renewable rather than depleting wherever technically and economically practicable.
8. Reduce derivatives – Unnecessary derivatization (blocking group, protection/deprotection, temporary modification) should be avoided whenever possible.
9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.
11. Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. Substances and the form of a substance used in a chemical process should be chosen to minimize potential for chemical accidents, including releases, explosions, and fires.

Trends

Attempts are being made not only to quantify the *greenness* of a chemical process but also to factor in other variables such as chemical yield, the price of reaction components, safety in handling chemicals, hardware demands, energy profile and ease of product workup and purification. In one quantitative study,[11] the reduction of nitrobenzene to aniline receives 64 points out of 100 marking it as an acceptable synthesis overall whereas a synthesis of an amide using HMDS is only described as adequate with a combined 32 points.

Green chemistry is increasingly seen as a powerful tool that researchers must use to evaluate the environmental impact of nanotechnology.[12] As nanomaterials are developed, the environmental and human health impacts of both the products themselves and the processes to make them must be considered to ensure their long-term economic viability.

Examples

Green solvents

Solvents are consumed in large quantities in many chemical syntheses as well as for cleaning and degreasing. Traditional solvents are often toxic or are chlorinated. Green solvents, on the other hand, are generally derived from renewable resources and biodegrade to innocuous, often naturally occurring product.[13][14]

Synthetic techniques

Novel or enhanced synthetic techniques can often provide improved environmental performance or enable better adherence to the principles of green chemistry. For example, the 2005 Nobel Prize for Chemistry was awarded, to Yves Chauvin, Robert H. Grubbs and Richard R. Schrock, for the development of the metathesis method in organic synthesis, with explicit reference to its contribution to green chemistry and "smarter production."[15] A 2005 review identified three key developments in green chemistry in the field of organic synthesis: use of supercritical carbon dioxide as green solvent, aqueous hydrogen peroxide for clean oxidations and the use of hydrogen in asymmetric synthesis.[16] Some further examples of applied green chemistry are supercritical water oxidation, on water reactions, and dry media reactions.

Bioengineering is also seen as a promising technique for achieving green chemistry goals. A number of important process chemicals can be synthesized in engineered organisms, such as shikimate, a Tamiflu precursor which is fermented by Roche in bacteria. Click chemistry is often cited as a style of chemical synthesis that is consistent with the goals of green chemistry. The concept of 'green pharmacy' has recently been articulated based on similar principles.[17]

Carbon dioxide as blowing agent

In 1996, Dow Chemical won the 1996 Greener Reaction Conditions award for their 100% carbon dioxide blowing agent for polystyrene foam production. Polystyrene foam is a common material used in packing and food transportation. Seven hundred million pounds are produced each year in the United States alone. Traditionally, CFC and other ozone-depleting chemicals were used in the production process of the foam sheets, presenting a serious environmental hazard. Flammable, explosive, and, in some cases toxic hydrocarbons have also been used as CFC replacements, but they present their own problems. Dow Chemical discovered that supercritical carbon dioxide works equally as well as a blowing agent, without the need for hazardous substances, allowing the polystyrene to be more easily recycled. The CO_2 used in the process is reused from other industries, so the net carbon released from the process is zero.

Hydrazine

Addressing principle #2 is the Peroxide Process for producing hydrazine without cogenerating salt. Hydrazine is traditionally produced by the Olin Raschig process from sodium hypochlorite (the active ingredient in many bleaches) and ammonia. The net reaction produces one equivalent of sodium chloride for every equivalent of the targeted product hydrazine:[18]

$$NaOCl + 2\ NH_3 \rightarrow H_2N\text{-}NH_2 + NaCl + H_2O$$

In the greener Peroxide process hydrogen peroxide is employed as the oxidant, the side product being water. The net conversion follows:

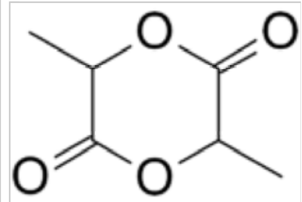
$$2\ NH_3 + H_2O_2 \rightarrow H_2N\text{-}NH_2 + 2\ H_2O$$

Addressing principle #4, this process does not require auxiliary extracting solvents. Methyl ethyl ketone is used as a carrier for the hydrazine, the intermediate ketazide phase separates from the reaction mixture, facilitating workup without the need of an extracting solvent.

1,3-Propanediol

Addressing principle #7 is a green route to 1,3-propanediol, which is traditionally generated from petrochemical precursors. It can be produced from renewable precursors via the bioseparation of 1,3-propanediol using a genetically modified strain of *E. coli*.[19] This diol is used to make new polyesters for the manufacture of carpets.

Lactide


Lactide

In 2002, Cargill Dow (now NatureWorks) won the Greener Reaction Conditions Award for their improved method for polymerization of polylactic acid . Unfortunately, lactide-base polymers do not perform well and the project was discontinued by Dow soon after the award. Lactic acid is produced by fermenting corn and converted to lactide, the cyclic dimer ester of lactic acid using an efficient, tin-catalyzed cyclization. The L,L-lactide enantiomer is isolated by distillation and polymerized in the melt to make a crystallizable polymer, which has some applications including textiles and apparel, cutlery, and food packaging. Wal-Mart has announced that it is using/will use PLA for its produce packaging. The NatureWorks PLA process substitutes renewable materials for petroleum feedstocks, doesn't require the use of hazardous organic solvents typical in other PLA processes, and results in a high-quality polymer that is recyclable and compostable.

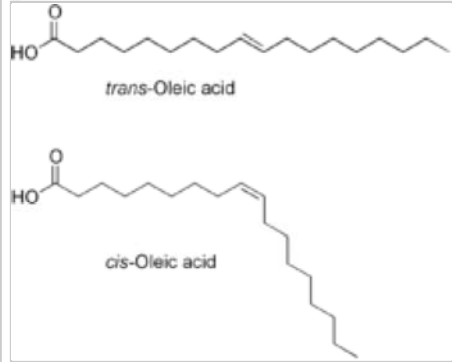
Carpet tile backings

In 2003 Shaw Industries selected a combination of polyolefin resins as the base polymer of choice for EcoWorx due to the low toxicity of its feedstocks, superior adhesion properties, dimensional stability, and its ability to be recycled. The EcoWorx compound also had to be designed to be compatible with nylon carpet fiber. Although EcoWorx may be recovered from any fiber type, nylon-6 provides a significant advantage. Polyolefins are compatible with known nylon-6 depolymerization methods. PVC interferes with those processes. Nylon-6 chemistry is well-known and not addressed in first-generation production. From its inception, EcoWorx met all of the design criteria necessary to satisfy the needs of the marketplace from a performance, health, and environmental standpoint. Research indicated that separation of the fiber and backing through elutriation, grinding, and air separation proved to be the best way to recover the face and backing components, but an infrastructure for returning postconsumer EcoWorx to the elutriation process was necessary. Research also indicated that the postconsumer carpet tile had a positive economic value at the end of its useful life. EcoWorx is recognized by MBDC as a certified cradle-to-cradle design.

Transesterification of fats

In 2005, Archer Daniels Midland (ADM) and Novozymes won the Greener Synthetic Pathways Award for their enzyme interesterification process. In response to the U.S. Food and Drug Administration (FDA) mandated labeling of *trans*-fats on nutritional information by January 1, 2006, Novozymes and ADM worked together to develop a clean, enzymatic process for the interesterification of oils and fats by interchanging saturated and unsaturated fatty acids. The result is commercially viable products without *trans*-fats. In addition to the human health benefits of eliminating *trans*-fats, the process has reduced the use of toxic chemicals and water, prevents vast amounts of byproducts, and reduces the amount of fats and oils wasted.

Bio-succinic acid



Trans and *cis* fatty acids

In 2011, the Outstanding Green Chemistry Accomplishments by a Small Business Award went to BioAmber Inc. for integrated production and downstream applications of bio-based succinic acid. Succinic acid is a platform chemical that is an important starting material in the formulations of everyday products. Traditionally, succinic acid is produced from petroleum-based feedstocks. BioAmber has developed process and technology that produces succinic acid from the fermentation of renewable feedstocks at a lower cost and lower energy expenditure than the petroleum equivalent while sequestering CO_2 rather than emitting it.[20]

Laboratory chemicals

Several laboratory chemicals are controversial from the perspective of Green chemistry. The Massachusetts Institute of Technology has created the [2] (http://ehs.mit.edu/site/content/green-chemical-alternatives-purchasing-wizard) to help identify alternatives. Ethidium bromide, xylene, mercury, and formaldehyde have been identified as "worst offenders" which have alternatives.[21] Solvents in particular make a large contribution to the environmental impact of chemical manufacturing and there is a growing focus on introducing Greener solvents into the earliest stage of development of these processes: laboratory-scale reaction and purification methods.[22] In the Pharmaceutical Industry, both GSK[23] and Pfizer[24] have published Solvent Selection Guides for their Drug Discovery chemists.

Legislation

The EU

In 2007, The EU put into place the Registration, Evaluation, Authorisation, and Restriction (http://ec.europa.eu/environment/chemicals/reach/reach_intro.htm) of Chemicals (REACH) program, which requires companies to provide data showing that their products are safe. This regulation (1907/2006) ensures not only the assessment of the chemicals' hazards as well as risks during their uses but also includes measures for banning or restricting/authorising uses of specific substances. ECHA, the EU Chemicals Agency in Helsinki, is implementing the regulation whereas the enforcement lies with the EU member states.

United States

The U.S. law that governs the majority of industrial chemicals (excluding pesticides, foods, and pharmaceuticals) is the Toxic Substances Control Act (TSCA) of 1976. Examining the role of regulatory programs in shaping the development of green chemistry in the United States, analysts have revealed structural flaws and long-standing weaknesses in TSCA; for example, a 2006 report to the California Legislature concludes that TSCA has produced a domestic chemicals market that discounts the hazardous properties of chemicals relative to their function, price, and performance.[25] Scholars have argued that such market conditions represent a key barrier to the scientific, technical, and commercial success of green chemistry in the U.S., and fundamental policy changes are needed to correct these weaknesses.[26]

Passed in 1990, the Pollution Prevention Act helped foster new approaches for dealing with pollution by preventing environmental problems before they happen.

In 2008, the State of California approved two laws aiming to encourage green chemistry, launching the California Green Chemistry Initiative. One of these statutes required California's Department of Toxic Substances Control (DTSC) to develop new regulations to prioritize "chemicals of concern" and promote the substitution of hazardous chemicals with safer alternatives. The resulting regulations took effect in 2013, initiating DTSC's *Safer Consumer Products Program*.[27]

Green Chemistry Education

Many institutions offer courses[28] and degrees on Green Chemistry. Examples from across the globe are Denmark's Technical University,[29] and several in the US, e.g. at the Universities of Massachusetts-Boston,[30] Michigan,[31] and Oregon.[32] A masters level course in Green Technology, has been introduced by the Institute of Chemical Technology, India. In the UK at the University of York[33] University of Leicester, Department of Chemistry and MRes in Green Chemistry at Imperial College London. In Spain different universities like the Universidad de Jaume I[34] or the Universidad de Navarra,[35] offer Green Chemistry master courses. There are also websites focusing on green chemistry, such as the Michigan Green Chemistry Clearinghouse at www.migreenchemistry.org (https://www.migreenchemistry.org//).
Apart from its Green Chemistry Master courses the Zurich University of Applied Sciences ZHAW presents an exposition and web page "Making chemistry green" for a broader public, illustrating the 12 principles.[36]

Scientific journals specialized in green chemistry

- *Green Chemistry* (RSC)
- *Green Chemistry Letters and Reviews (http://www.tandfonline.com/tgcl)* (Open Access) (Taylor & Francis)
- ChemSusChem (http://onlinelibrary.wiley.com/journal/10.1002/(ISSN)1864-564X) (Wiley)
- ACS Sustainable Chemistry & Engineering (http://pubs.acs.org/journal/ascecg) (ACS)

Contested definition

There are ambiguities in the definition of green chemistry, and in how it is understood among broader science, policy, and business communities. Even within chemistry, researchers have used the term "green chemistry" to describe a range of work independently of the framework put forward by Anastas and Warner (i.e., the 12 principles).[9] While not all uses of the term are legitimate (see greenwashing), many are, and the authoritative status of any single definition is uncertain. More broadly, the idea of green chemistry can easily be linked (or confused) with related concepts like green engineering, environmental design, or sustainability in general. The complexity and multifaceted nature of green chemistry makes it difficult to devise clear and simple metrics. As a result, "what is green" is often open to debate.[37]

Green Chemistry Awards

Several scientific societies have created awards to encourage research in green chemistry.

- Australia's Green Chemistry Challenge Awards overseen by The Royal Australian Chemical Institute (RACI).
- The Canadian Green Chemistry Medal.[38]
- In Italy, Green Chemistry activities center around an inter-university consortium known as INCA.[39]
- In Japan, The Green & Sustainable Chemistry Network oversees the GSC awards program.[40]
- In the United Kingdom, the Green Chemical Technology Awards are given by Crystal Faraday.[41]
- In the US, the Presidential Green Chemistry Challenge Awards recognize individuals and businesses.[42][43]

See also

- *Green Chemistry* (journal) – published by the Royal Society of Chemistry
- Green chemistry metrics
- Sustainable engineering
- Green engineering
- Environmental engineering science
- Green computing – a similar initiative in the area of computing
- Bioremediation – a technique that generally falls outside the scope of green chemistry

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